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(54) Method for the rehabilitation of a crystallizer of a continuous casting ingot mould.

(57) Method to rehabilitate the inner surfaces of a crystallizer of an ingot mould and/or the plates forming a crystallizer of an ingot moulds by means of an electrolytic treatment, whereby those surfaces undergo steps of preparation, cleaning, copper plating and finishing, the method comprising the following successive steps:

a) elimination of scoring (2) of those surfaces,

b) milling or grinding the surfaces,

c) removal of grease or oily products from the surfaces,

d) covering the surfaces not about to undergo copper plating with a material (3) inert to the electrolytic treatment,

e) anodic electrolysis in a basic solution and activation in an acid solution,

f) copper plating in a galvanic bath (11),

g) withdrawal of the crystallizer and/or the plates from the galvanic bath and removal of the inert material (3), and

h) grinding of the copper plated surfaces.

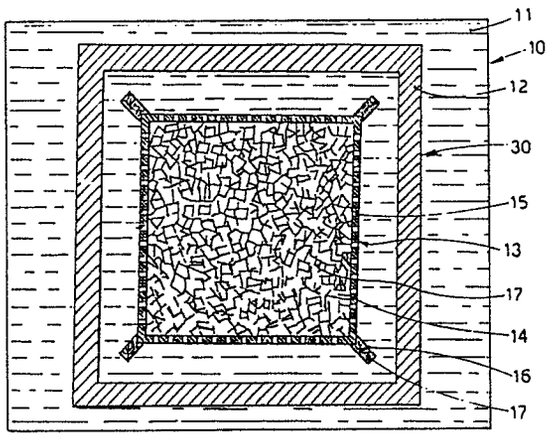

Fig.7

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"METHOD FOR THE REHABILITATION OF A CRYSTALLIZER OF A CONTINUOUS CASTING INGOT MOULD"

This invention concerns a method for the rehabilitation of a crystallizer employed in plants carrying out the continuous casting of steel or other products.

As is known, the molten metal coming from a smelting furnace and collected in a ladle is passed through one or more ingot moulds suitably arranged to obtain superficial cooling of the molten mass; the cooling thereafter proceeds during the successive casting steps.

A continuous casting ingot mould consists of a steel cooling jacket, in which a cooling liquid (usually water) is circulated, and of an inner tubular assembly, which comes into contact with the incandescent mass and is called a "crystallizer".

This crystallizer is usually made of copper and may consist of one single piece or of suitably dimensioned plates placed side by side. It has to be shaped also with its lower end tapered so as to take account of the progressive dimensional shrinkage of a bar while cooling.

Being in contact with the molten mass at a very high temperature and with the solidified skin of the metal being cast, the crystallizer undergoes considerable wear and therefore after a given number of working cycles, can be employed no longer and has to be replaced with a new crystallizer.

At the present time a crystallizer thus replaced is sent out as scrap or is rehabilitated if its state of conservation so permits.

To be more exact, if it is to be rehabilitated, it must have retained the following required features:

a) the typical original hardness of the copper alloy of which it consists,

b) it must be free of deep cracks, and

c) it must be devoid of significant geometric deformations.

One known rehabilitation system is based on mechanical pressing; in fact, the crystallizer is compressed uniformly about a gauge which has outer dimensions the same as the corresponding inner dimensions of the crystallizer.

The inner surface of the crystallizer is restored by means of this system, but its thickness is reduced thereby so that a play between the outer wall of the crystallizer and the inner wall of the cooling jacket surrounding the crystallizer is produced which is such as to prevent perfect contact between those walls.

Thus, an ingot mould equipped with such a crystallizer, which is not sufficiently in contact with the cooling jacket, is unlikely to be able to ensure a good progress of the casting.

Document DE-A-2.936.177 discloses a process for the treatment of the walls of a crystallizer by means of galvanic or electrolytic solutions.

This process can only be employed with crystallizers having their walls consisting of separable plates, each of which is supported on a frame, cooling channels being provided in the walls.

The crystallizer wall thus conformed is supported on the inner surface of a first container suitable to be filled with a galvanic solution. This first container is provided with an anode positioned in front of the inner wall of the crystallizer and is connected to a second container which recovers and heats the solution.

The process described in this document does not provide for any treatment of the inner wall of the crystallizer nor, in particular, for any treatment of the copper wall which is to receive the casting of molten metal ; instead, it provides for a treatment of the outer surfaces of the plates.

Moreover, this process requires a special arrangement of the plates on the first container and is not suitable for the treatment of a whole crystallizer in one single electro-deposition.

Document DE-A-3.231.444 discloses a process for the rehabilitation of crystallizers made of copper or a nickel-based copper alloy in which the layer of nickel is removed and a new layer of nickel covers the copper.

This process provides for the filing of a part of the layer of nickel, an alkaline degreasing bath and an acid activating bath based on sulphuric or phosphoric acid. Another layer of nickel is deposited thereafter on the surface thus freed.

This document does not provide for rehabilitation of crystallizers in which the copper layer below the nickel also contains corrosion and/or scoring.

In view of such state of the art the purpose of this invention is to rehabilitate an ingot mould crystallizer and/or the plates of which it consists by restoring its inner surfaces perfectly and leaving its outer surfaces unchanged.

This purpose is achieved by a method to rehabilitate the inner surfaces of an ingot mould crystallizer and/or the plates forming the walls of an ingot mould crystallizer according to Claim 1.

The dependent claims describe preferred forms of accomplishing this method.

The method according to this invention provides for the following steps of preparation and thorough cleaning:-

a) elimination of scoring, even if deep, on the inner surfaces of the crystallizer,

b) milling or grinding the inner surfaces of the crystallizer;

c) removal of grease or oily products from all the surfaces of the crystallizer,

d) covering the surfaces not to undergo copper plating with a material inert to electrolytic treatment, and

e) anodic electrolysis in a base solution and activation in an acid solution.

Moreover, the method according to the invention provides for the following finishing steps on the crystallizer after the copper plating:

f) withdrawal of the crystallizer from the galvanic bath and removal of the inert material used to cover the surfaces which were not to undergo copper plating, as in point d) above, and

g) grinding the copper plated surfaces.

A further plating step with the electrodeposition of other metals may be included with the purpose of prolonging as much as possible the working life of the crystallizer thus rehabilitated in the subsequent re-use thereof in continuous casting plants.

All the steps of the method will now be disclosed in detail with reference to the attached drawings, in which:-

Figs.1 to 4 give diagrams of a crystallizer in the steps of the method which cover the preparation and thorough cleaning before the main copper plating step;

Fig.5 gives a plan view of the crystallizer immersed in an electrolysis vessel in a base solution;

Fig.6 gives a plan view of the crystallizer immersed in an electrolysis vessel in an acid solution;

Fig.7 shows a plan view of the copper plating step in an electrodeposition vessel;

Fig.8 gives a side view of an anode of Fig.7;

Fig.9 shows another type of anode which can be used as an alternative to that of Fig.7;

Figs.10 and 11 show the crystallizer in the steps which follow the copper plating.

As said earlier, the crystallizer must be checked first of all to ensure its suitability for rehabilitation.

In fact, it is necessary that the typical hardness of the copper alloy of which the crystallizer consists should have been retained and that there should be no cracks deeper than 50% of its thickness; any scoring, even if deep, is remedied with a preliminary step of elimination of the scoring by buffing and subsequent soldering, with the use of copper alloys and appropriate methods.

At the end of this step, a crystallizer 30, which may be tubular with a square section as shown in Fig.1, for instance, has inner scoring 2 filled with soldered metal.

Its shape and dimensions will obviously vary on each occasion, depending on the type of crystallizer being examined.

There follows a step of milling the surfaces of the crystallizer which are to be copper plated so as to eliminate unevenness 1 due to its previous use and to the process of laying copper alloy in the scoring.

At the end of this step the crystallizer has its inner surfaces smooth, as shown in Fig.2.

Next, it is necessary to remove from the inner surfaces any residues of grease and oily substances and to cover with a material inert to the electrolytic process the surfaces which are not to be copper plated.

Fig.3 shows a crystallizer of which the surface covered with an inert film material 3 is marked with dashes.

The surfaces to be copper plated are honed next to remove any strains due to the earlier mechanical processes and to impart to the surfaces the proper roughness (Fig.4) for fixture of the player of copper.

At the end of the above step the crystallizer 30 undergoes anodic electrolysis in a base solution 31 with the use of an anode 33 (Fig.5) and thereafter is activated in an acid solution 32 with the use of an anode 34 (Fig.6).

The anodic electrolysis eliminates saponifiable fats from the surface, whereas the activation eliminates any traces of oxide, thus making the surfaces active and putting the grains of copper in the crystallizer into the best condition for being bonded with the new layer which will be electrodeposited on those grains.

Next, there follows the step of depositing the layer of copper (Fig.7) by electrodeposition in a vessel 10 containing a bath 11, anode 13 and a cathode 12.

The cathode 12 consists of the crystallizer itself, while the anode 13 is a suitably shaped titanium frame.

The frame shown in Fig.7 has been dimensioned for a crystallizer having an almost square shape and comprises a tubular portion 14 the walls of which are provided with a plurality of holes 15 (Fig.8) and with protrusions 16, which also contain holes and are arranged like a spider of spokes about the tubular portion 14.

The inside of the tubular portion 14 and the spokes 16 are filled with small blocks 17 of copper shaped as cubes or disks.

According to a variant shown in Fig.9 the anode 13 consists of a titanium frame which, instead of containing blocks of copper, is coated with an adequate layer of copper 18.

It is also possible to use rolled and shaped copper bars as an anode.

Naturally, a suitable round anode will be employed with round tubular crystallizers, while it will be enough to place the crystallizer plates in front of

anodes which may consist of a set of titanium baskets filled with copper cubes or of copper bars of a suitable chemical composition.

The bath 11 prepared in the vessel 10 holds the following compounds, of which the respective fields of values of the contents are given:

- copper suphate ($CuSO_4 \times 5H_2O$) from 150 to 280 grs/lt
- sulphuric acid (H_2SO_4) from 30 to 90 grs/lt
- antipitting agent from 0.3 to 0.8 gr/lt
- anode activation and polishing agent from 0.3 to 0.8 gr/lt

For instance, a typical bath will contain the following quantities of the above compounds:

- copper sulphate ($CuSO_4 \times 5H_2O$) about 220 grs/lt
- sulphuric acid (H_2SO_4) about 70 grs/lt
- antipitting agent about 0.4 gr/lt
- anode activation and polishing agent about 0.4 gr/lt

The copper sulphate makes available the cupric ions (Cu^{++}) required for the electrodeposition.

The sulphuric acid prevents the formation of base copper salts which would form a very friable coating, and also increases the conductivity of the bath and assists the formation of fine-grain deposits.

The antipitting agent performs the action of reducing the surface tension of the bath and enhances the levelness of the layer deposited.

The activation agent reduces the sizes of the grains and has a depolarising effect on the copper anodes.

Other conditions laid down for the bath are:

- a temperature ranging between 20° and 40°C;
- current density from 3 to 10 A/sq.dm.

Stirring with air and a continuous filtration of the bath are also necessary.

The average conditions of a typical bath will be, for instance, as follows:

- temperature 30 ± 10°C
- current density 6 A/sq.dm.
- stirring with air 0.2 lt/min. per litre of inner volume of the crystallizer
- continuous filtration 10 μ.

After having prepared the bath 11 in the electrodeposition vessel 10, steps are taken to wrap the anode 13 in a Meraclon, Terylene or polypropylene, etc. cloth so as not to pollute the bath; the anode is then placed within the crystallizer to be copper plated, and the whole is immersed in the vessel 10.

When current is applied, the copper in the copper sulphate solution is deposited on the cathode and the copper in the solution thus consumed is balanced by dissolution of the anode.

The length of the duration of this process will vary according to the thickness of the layer of the copper to be restored but it will generally last between ten and twenty hours.

It is necessary to arrange for the duration of the electrodeposition to be such that the layer deposited is thicker than the final layer required, this being necessary for the purposes of the successive processes. In general an excess of at least 0.2 to 0.3 mm. per surface is required.

During the electrodeposition, as the anode efficiency is greater than the cathode efficiency and if we also take into account the composition of the bath 11, the concentration of copper ions will increase, and therefore at the end of each electrodeposition process it is best to remove the anode 13 or anodes from the bath.

After the copper plating, which is carried out in one depositing step, the inert material 3 covering the surfaces not copper plated is removed and the crystallizer then undergoes grinding to obtain the exact dimensions required.

At the end of the grinding step the crystallizer will be as shown in an end view in Fig.10.

The line of dashes 21 and continuous line 22 indicate diagrammatically the profile of the crystallizer before the electrodeposition step, whereas the inner continuous line 23 indicates the final inner profile. The overall crystallizer is referenced with 30.

The method provides also, preferably, before removal of the inert material 3, a further final step of internal coating to give the crystallizer better properties.

A first type of coating consists of nickel plating followed by chromium plating.

Another type of coating arranges to interpose, between the nickel plating and chromium plating, an electrodeposition of a layer of an alloy consisting of nickel and phosphorus; this alloy possesses excellent abrasion resistance and, through thermal effect, reaches more than 70° Rockwell hardness.

The crystallizer shown in Fig.11 is the final product obtained with the method described; the reference No.20 in this figure indicates the final multiple coating.

Claims

1 - Method to rehabilitate the inner surface of a crystallizer of an ingot mould and/or the plates forming a crystallizer of an ingot moulds by means of an electrolytic treatment, whereby those surfaces undergo steps of preparation, cleaning, copper plating and finishing, the method being characterized in that it comprises the following successive steps:

a) elimination of scoring (2) of those surfaces,

b) milling or grinding the surfaces,

c) removal of grease or oily products from the surfaces,

d) covering the surfaces not about to undergo copper plating with a material (3) inert to the electrolytic treatment,

e) anodic electrolysis in a base solution and activation in an acid solution,

f) copper plating in a galvanic bath (11),

g) withdrawal of the crystallizer and/or the plates from the galvanic bath and removal of the inert material (3), and

h) grinding of the copper plated surfaces.

2 - Method as claimed in Claim 1, in which after the step of grinding the copper plated surfaces a further step of final coating of the crystallizer is included, such coating (20) being produced with other metals by electrodeposition.

3 - Method as claimed in Claim 2, in which the electrolytically deposited metals forming the final coating are nickel and chrome.

4 - Method as claimed in Claim 3, in which an electrolytically deposited layer of an alloy of nickel and phosphorus is interposed between the electrolytically deposited layers of nickel and chrome.

5 - Method as claimed in Claim 1, in which the copper plating step provides for the preparation of an electrodeposition vessel (10) containing the bath (11), in which a cathode (12) consists of the crystallizer to be rehabilitated, whereas an anode (13) consists of a support able to release cupric ions into the bath (11).

6 - Method as claimed in Claim 5, in which the anode (13) consists of a titanium frame having a tubular portion (14) the walls of which comprise a plurality of holes (15), the holes being included also in protrusions (16) arranged like a spider of spokes about the tubular portion (14), the inside of the tubular portion (14) and of the protrusions (16) being filled with copper blocks (17).

7 - Method as claimed in Claim 5, in which the anode (13) consists of a titanium frame coated with an adequate layer of copper (18).

8 - Method as claimed in Claim 5, in which the anode (13) consists of rolled and shaped copper bars.

9 - Method as claimed in Claim 1, in which the bath (11) contains the following compounds:
- copper suphate ($CuSO_4 \times 5H_2O$) in quantities from 150 to 280 grs/lt
- sulphuric acid (H_2SO_4) in quantities from 30 to 90 grs/lt
- antipitting agent in quantities from 0.3 to 0.8 gr/lt
- anode activation and polishing agent in quantities from 0.3 to 0.8 gr/lt,

the bath undergoing continuous filtration and stirring with air, its physical conditions being as follows:
- temperature from 20° to 40°C,
- current density from 3 to 10 A/sq.dm.

10 - Method as claimed in Claim 5, in which the length of the duration of the electrodeposition will vary according to the required thickness of the copper electrolytically deposited.

11 - Method as claimed in any of Claims 5, 8 and 10, in which the length of duration of the electrodeposition will vary from about 10 to 20 hours.

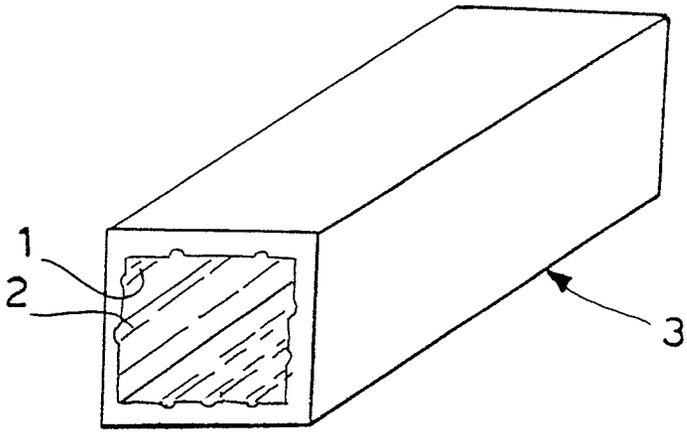


Fig.1

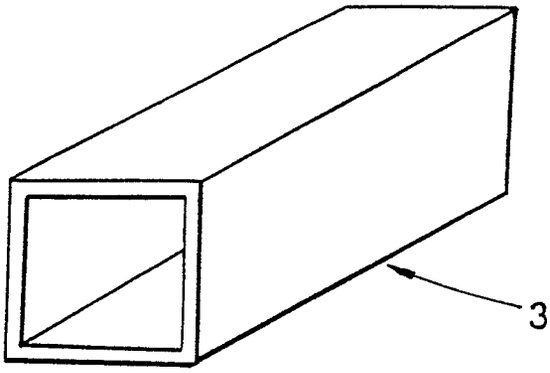


Fig.2

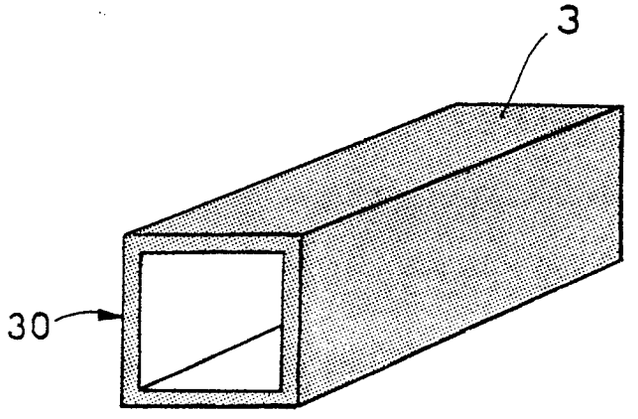


Fig.3

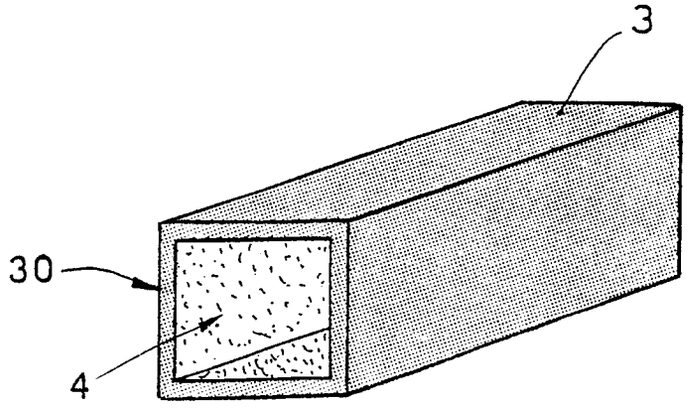


Fig.4

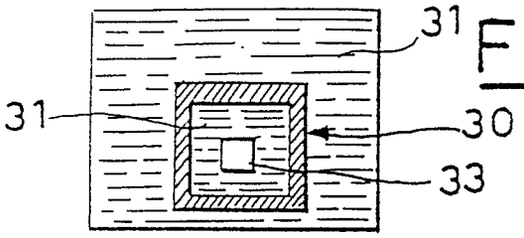


Fig.5

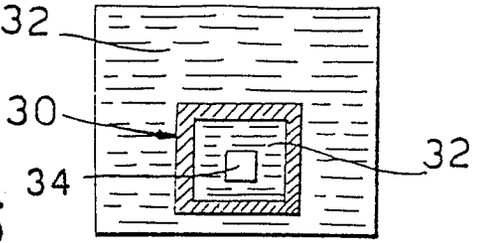


Fig.6

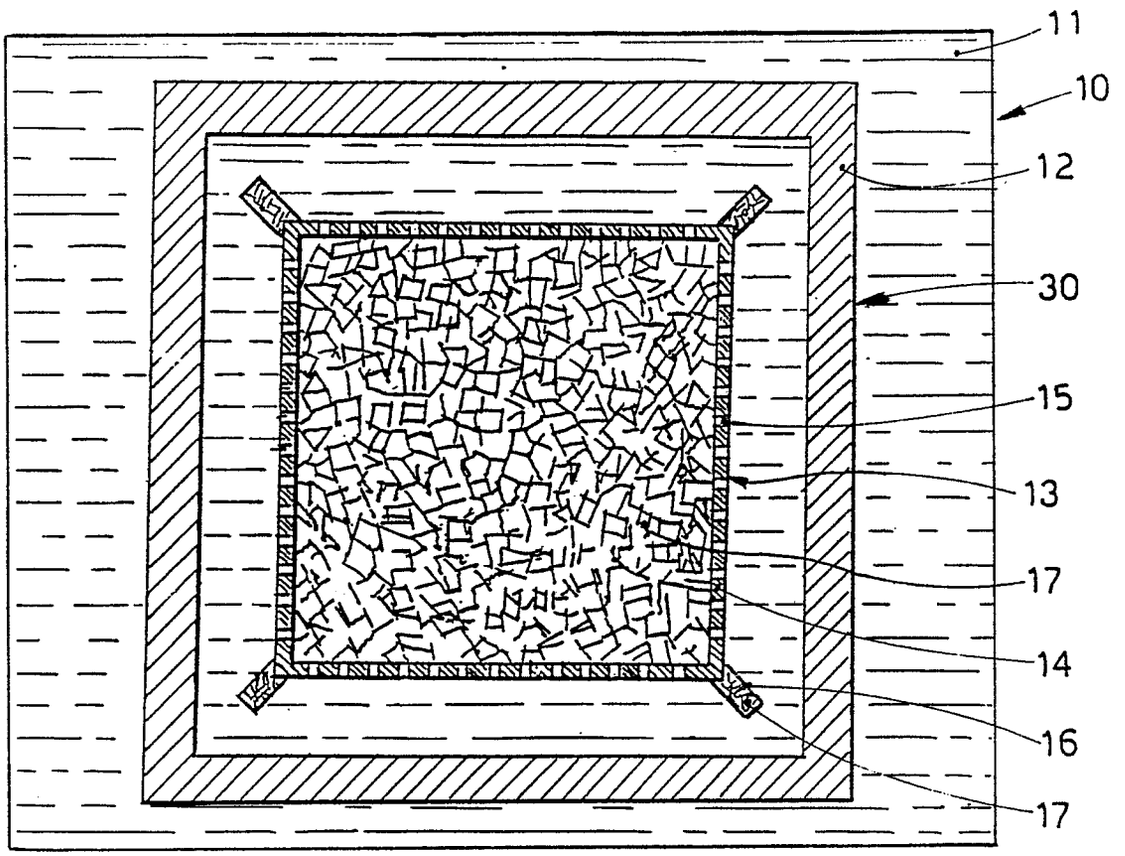


Fig.7

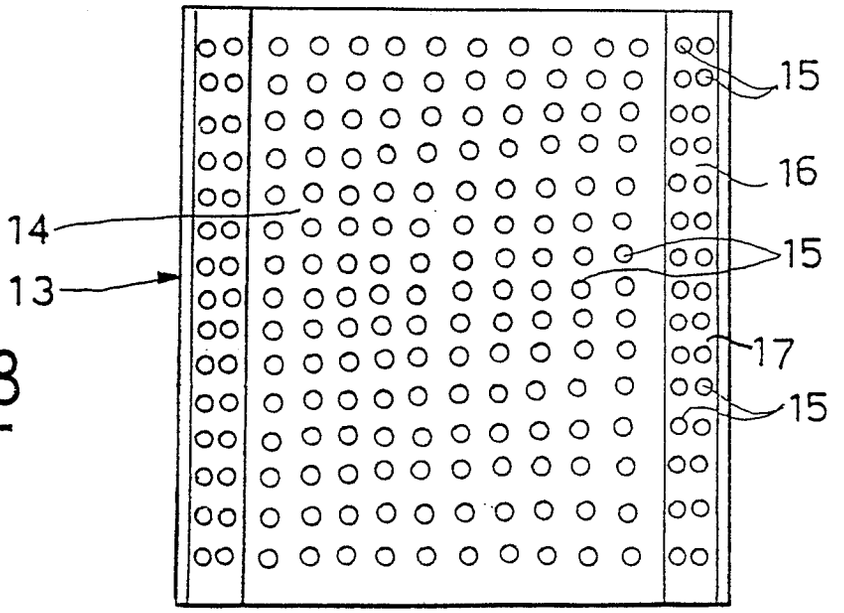


Fig.8

Fig.9

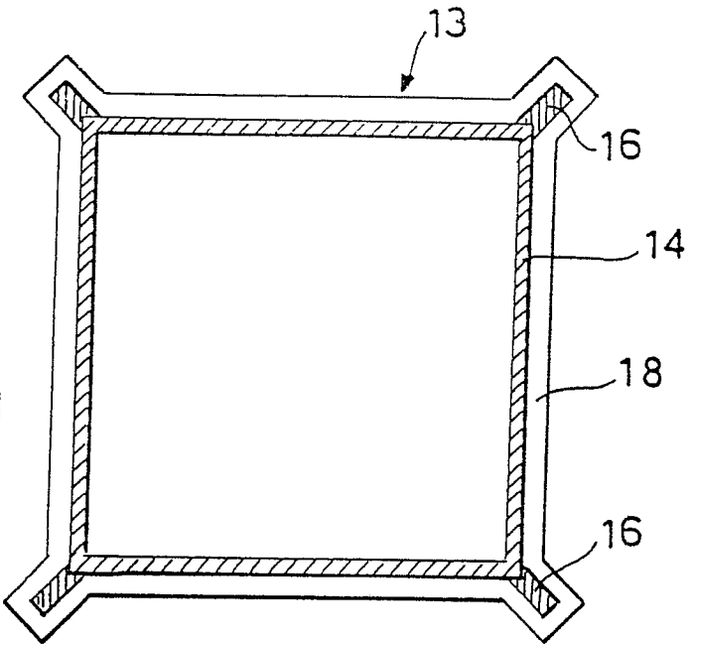


Fig.10

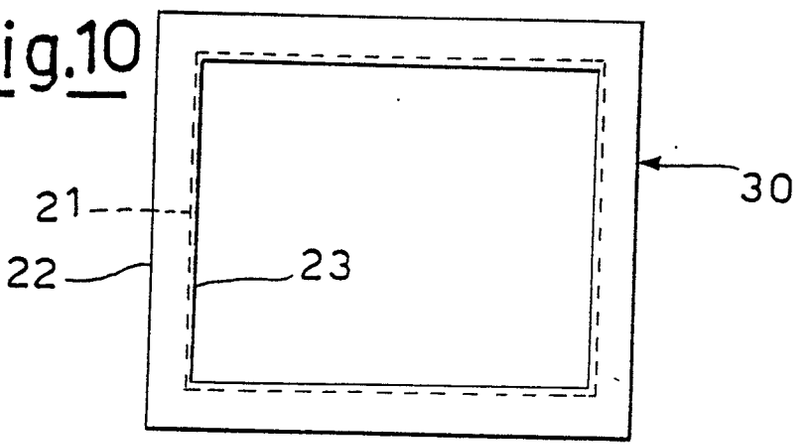
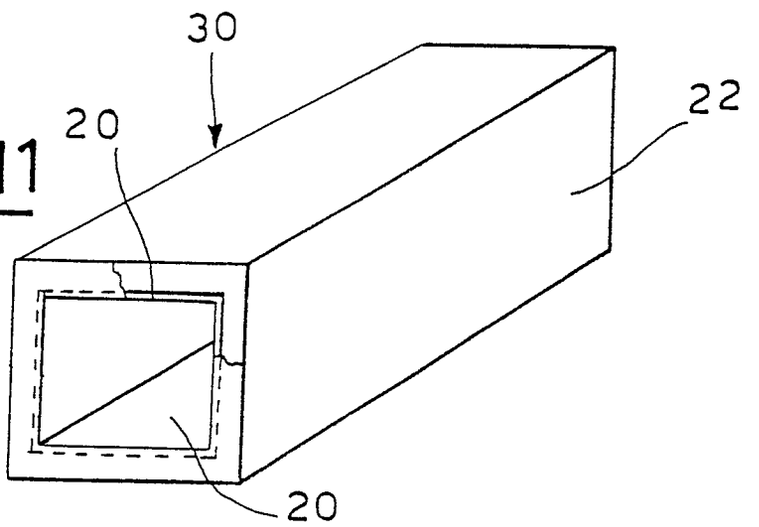


Fig.11



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EUROPEAN SEARCH REPORT

Application Number

EP 88 10 2498

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 45 (M-118)[923], 20th March 1982; & JP-A-56 160 857 (NOMURA TOKIN K.K.) 10-12-1981 * Whole abstract *	1,5,8-11	B 22 D 11/04
Y	IDEM	2-4,6	
Y	DE-A-3 215 689 (SUMITOMO METAL INDUSTRIES) * Page 12, line 5 - page 14, line 23 *	2-4	
Y	J.K. DENNIS et al.: "Nickel and chromium plating", 1972, pages 65-66, Newnes, Butterworths, London, GB * Pages 65,66, figure 4.4 *	6	
Y	DE-A-2 063 632 (SIFCO INDUSTRIES INC.) * Page 6, line 17 - page 11, line 11 *	1	
Y,D	DE-A-3 231 444 (NIPPON STEEL CORP.) * Claims 1-2,5 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US-A-3 186 925 (J. KUSHNER) * Column 1, lines 16-27; column 4, lines 22-26 *	1,9	B 22 D
A	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 169 (M-231)[1314], 26th July 1983; & JP-A-58 74 252 (MISHIMA KOUSAN K.K.) 04-05-1983 * Abstract *	3-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21-06-1988	DOUGLAS K.P.R.

CATEGORY OF CITED DOCUMENTS

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